## PATENT SPECIFICATION

(11) 1424517

TERR

(21) Application No. 35913/72

(22) Filed 1 Aug. 1972

(23) Complete Specification filed 20 July 1973

(44) Complete Specification published 11 Feb. 1976

(51) INT CL<sup>8</sup> C09B 67/00//C08F 8/00 C09B 67/00

(52) Index at acceptance

C3P D9AX D9D7D2 D9D8 D9F1 C3R 27C 27K8E C11 C12 C13M C14B C16 C21 L2X C4A K

(72) Inventors ARTHUR TOPHAM and MORICE WILLIAM THOMPSON



(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Milibank, London S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to dispersions of

This invention relates to dispersions of 10 organic pigments in solvent media containing dissolved therein dispersing agents,

According to the invention there is provided a dispersion of an organic pigment in a solvent containing, dissolved therein, a dispersing agent of the formula:—

$$D-(Z-R)_n$$

wherein D is the radical of a dyestuff which is attached to Z through a carbon atom of an aromatic ring present in D; Z is a divalent 20 bridging group; n is a positive integer having a value of from I to 8; and R is the residue of an optionally-substituted addition polymer chain.

The dyestuff radical represented by D can be a radical of any of the known dyestuff series, such as an azo or anthraquinone radical but more particularly D is a phthalocyanine radical especially a radical of copper phthalocyanine. D is preferably free from strongly acidic groups such as carboxylic acid and sulphonic acid groups.

The nature of the divalent bridging group represented by Z is not critical, and as examples of such groups there may be mentioned especially

and

40 and also

nd —NH—CH<sub>2</sub>—CH<sub>2</sub>— —NH—CO—CH<sub>2</sub>.

The residue R may be derived from any addition polymer or copolymer which may optionally carry one or more substituent groups, the polymer chain of R being attached to the linking group Z either directly or through a substituent group. The residue R preferably contains a polymer chain which is solvatable, this term being used in the sense it is used in Specifications 1,108,261 and 1,096,912. The term "solvatable" implies that the chain can exit in an extended molecular state in a solvent medium, in particular in the solvent medium in which the dispersing agent is to be used. This normally requires that the polarity of the solvent medium and of the solvatable polymer chain should be similar, or that there be some chemical or physical interaction, e.g. hydrogen bonding, between the solvent and the polymer chain. In general the polarity of the polymer chain will depend upon the nature of other atoms or groups attached to, or present in, the basic chain structure and may be tailored to fit the chosen solvent medium.

Suitable additon polymers include polyalkylene oxides, as listed for example in Specification No. 1,108,261 on page 2 in lines 26—28, and which may contain for example an aryloxy end-group and, especially, polymers and copolymers of ethylenically unsaturated monomers. Examples of the latter classes of polymers may be found in Specification No. 1,108,261 on page 2 in lines 39—91 and Specification No. 1,096,912 on page 3 in lines 20—34.

The dispersing agent of the formula: -

$$D$$
— $(Z$ — $R)_n$ 

80

can be prepared by a process which comprises reacting a modified dyestuff compound of the formula

$$D \rightarrow (Z \rightarrow Y)_n$$

wherein D, Z and n have the meanings stated and Y is a chlorine or a bromine atom, with one or more polymers of the formula R—H wherein R has the meaning hereinbefore stated and H is a replaceable hydrogen atom.

The conditions under which the process is carried out will depend in particular upon the nature of the group —Z—Y and on the nature of the hydrogen atom in the polymer R—H.

In a preferred form of the process Z is a methylene group and the hydrogen atom is contained in a carboxyl group as for example in the polymers of Specification 1,096,912. In this preferred process the reactants may be 15 stirred together in inert organic liquid such as a hydrocarbon or chlorinated hydrocarbon at a temperature up to the boiling point of the reaction medium. The reaction is preferably effected in presence of an acid-binding agent and a quaternary ammonium or phosphonium compound. The reaction is preferably carried out under anhydrous conditions, and, in the event that water is formed in the reaction or any of the reactants contain water or are used in the form of aqueous solutions it is advisable to carry out the reaction at such a temperature that the water present distils off from the reaction medium. At the conclusion of the reaction the organic liquid can be removed, 30 for example by distillation; or the mixture may be filtered, the filtrate extracted with water to remove the quaternary ammonium or phosphonium compound and any inorganic salts present, and then with a solvent such as iso-35 butancl to remove any unreacted polymer, and the organic liquid then removed, for example by distillation or evaporation.

When the quaternary ammonium or phosphonium compound is a quaternary ammonium hydroxide then, provided that sufficient is present, this also acts as the acid-binding agent. However, the quaternary ammonium or phosphonium compound is normally used as a catalyst for the reaction, so that whilst stoichic metric amounts can be added if desired, the use of such large amounts is in fact unnecessary, and amounts in the region of 1 to 30% based on the weight of modified

dyestuff compound are adequate.

As examples of organic liquids which can be used in the process there may be mentioned ketones such as methyl isobutyl ketone, hydrocarbon liquids such as petroleum fractions, teluene and xylene, and halogenated bydrocarbons with an unreactive halogen atem

such as chlorobenzene.

As examples of quaternary ammenium or phosphonium compounds there may be mentioned cetyl trimethylammonium bromide, tetraethyl ammoniumhydroxide, dodecyltrimethylammonium bromide and n-hexadecyl tri-n-propylphosphonium bromide.

The modified dyestuff compounds which can be used in the process can themselves be prepared by standard known methods for the introduction of groups of the formula:

## --Z-Y

into dyestuff compounds. Thus, for example, chloremethyl or bremomethyl groups can be introduced by treating the appropriate dyestuff compound with formaldehyde or paraformaldehyde in the presence of hydrogen chloride, chlorosulphonic acid or hydrogen bromide,  $\gamma$ -chloro- $\beta$ -hydroxypropylamino or  $\gamma$ -bromo- $\beta$ -hydroxypropylamino groups can be introduced by reacting the corresponding dyestuff containing an amino group with epichlorohydrin or with epibromehydrin, and N - (chlorocr bromoalkyl) sulphonamido groups can be introduced by treating the appropriate dyestuff compound with chlorosulphonic acid and reacting the resulting sulphonchloride with a chloro- or bromo- alkylamine.

As specific examples of the modified dyestuff compounds containing at least one reactive chlorine or bromine atom there may be mentioned copper tris(chloromethyl)phthalocyanine, 1:4 - bis( $\gamma$  - chloro -  $\beta$  - hydroxypropylamino)anthraquinone, 2 - methyl - 4-N:N - di( $\beta$  - hydroxyethyl)amino - 4' - (N- $\beta$  - chloro-thyl sulphonamido) - azobenzene, 1 - ( $\gamma$  - chloro -  $\beta$  - hydroxypropylamino) - 4-[4' -  $\beta$  - hydroxyethexy phenylamino]anthraquinone, copper mono(chloromethyl)-phthalocyanine and copper pentakis - (chloromethyl)phthalocyanine.

In an alternative process for the preparation of the dispersing agent wherein the polymer R—H is an aryloxy - terminated polyalkylene exide the reaction is carried out by heating the stirred reactants in presence of a Friedel-Crafts catalyst such as zinc chloride.

As exampples of suitable dispersing agents there are mentioned compounds of the formula

$$D-(Z-R)_n$$
 105

wherein D is a copper phthalocyanine residue, Z is a methylene group, n is 3 and R is a group of the formula

of number average molecular weight 2500, the polymer chain being obtained by the polymerisation of methyl methacrylate, or R is a group of the formula

of number average molecular weight 2300, 3800 or 8600, the polymer chain being obtained by the polymerisation of styrene, or R is a group of the formula

of number average molecular weight 2900, the polymer chain being a random copolymer chain from 70% by weight of lauryl methacrylate and 30% of styrene, or R is a group of the formula

or wherein n is 5 and R is a group of the formula

10 of number average molecular weight 3800, or wherein D is a p.p' - bis - (6 - methylbenz-thiazol - 2 - yl)azobenzene residue, Z is a methylene group, n is 2, and R is a group of the formula

of number average molecular weight 3800, or wherein D is a  $1 - [p - (\beta - hydroxyethoxy) - anilino]$  anthraquinone residue, Z is a group of the formula

n is 1, and R is a group of the formula

of number average molecular weight 3800, or wherein D is a 2 - methyl - 4 - (N,N - bis-20  $\beta$  - hydroxyethylamino)benzeneazobenzene residue, Z is a group of the formula

n is 1, and R is a group of the formula

of number average molecular weight 3800.

In preparing the dispersions of the invention it has been found that it is not essential to use pure dispersing agents since dispersing agents obtained by the above described process, which initially contain in-30 organic salts, quaternary ammonium or phosphonium compound and any unreacted polymer are equally suitable as it has been found that the presence of such compounds does not adversely affect the formation of the disper-35 sions. Accordingly this reduces the cost of the dispersing agents by removing the necessity for purifying them. In fact when the dis-persing agent has been prepared in a suitable solvent medium the resulting solution of the 40 dispersing agent can be used directly for the preparation of the dispersion without even the necessity to remove the solvent medium.

The said dispersions can be obtained by any of the conventional and well known methods of preparing dispersions. Thus the organic pigment, the solvent medium and the dispersing agent may be mixed in any order and the mixture then subjected to a mechanical treatment to reduce the particle size of the organic pigment, for example by ball milling, bead milling or gravel milling until the dispersion is formed. Preferably the mechanical treatment is carried out until the particule size of the organic pigment is less than 20 microns and preferably less than 10 microns

If desired, the dispersion can contain other substances, such as zinc resinate, which are conventionally present in dispersions of organic pigments in organic liquids.

60

Alternatively, the organic pigment can be treated to reduce its particle size independently or in admixture with either the solvent medium or the dispersing agent, and the other ingredient or ingredients then added following which dispersion can be obtained by stirring the mixture. As a further alternative a solution of the dispersing agent in an organic solvent medium can be emulsified into an

aqueous phase by known means, such as high speed stirring, in the presence of one or more surface active agents, and the resulting emulsion added to an aqueous slurry of the organic pigment, after which the organic solvent medium and the water are removed by filtration and drying of the residue of organic pigment and dispersing agent. This residue can be subsequently dispersed in an organic 10 medium. Compositions obtained in this way and comprising the organic pigment in finely divided form and the dispersing agent are a further feature of the invention.

It is preferred that the amount of dispersing 15 agent present in the dispersions is such as corresponds to between 5 and 100% by weight, and preferably between 10 and 30%, based on the weight of the organic pigment, and the dispersions preferably contain from 5 to 70% by weight of the organic pigment based on the total weight of the dispersion.

The solvent medium used to prepare the said dispersions can be any inert solvent medium or mixture of solvent media in which 25 the said dispersing agents are at least partly soluble at ambient temperatures and which is stable under the subsequent conditions of usage of the dispersion. The preferred solvent media are organic solvents especially hydrocarbons and halogenated hydrocarbons such as benzene, toluene, xylene, white spirit, nhexane, cyclohexane, chlorobenzene, chloro-form, carbon tetrachloride, and perchloro-ethylene. Other organic liquids can however 35 be used, for example exters such as alkyd resins, heat bodied linseed oils used as lithographic varnish media and acids such as acetic acid. It is however especially preferred that the organic liquid is a predominantly ali-40 phatic petroleum fraction. In general, the organic solvents or mixtures thereof used to prepare the dispersions will depend on the subsequent uses to which the dispersions are to be put. Inorganic solvent media, particularly 45 water or aqueous media, may however be used.

The organic pigments can be any of the recognised classes of organic pigments.

As examples of such organic pigments 50 there may be mentioned pigments of the azo, thioindigo, anthraquinone, anthanthrene, iso-dibenzanthrone or triphendioxazine series, vat dye pigments, phthalocyanine pigments such as copper phthalocyanine and its nuclear halogenated derivatives and copper tetraphenyl and octaphenyl phthalocyanines, quinacridone pigments and lakes of acid, basic and mordant dyestuffs. Such pigments are described in, for example, volume 2 of the 2nd Edition of the 60 Colour Index which was published in 1956 under the heading "Pigments" and in subsequent authorised amendments thereto. Preferred pigments are copper phthalocyanine and its nuclear halogenated derivatives. When 65 the pigment is B-form copper phthalocyanine

it may be the normal pigmentary form of the copper phthalocyanine or it may be crude

copper phthalocyanine.
The dispersing agents are particularly valuable for the preparation of pigmentary dispersions of copper phthalocyanine directly from crude copper phthalocyanine. A preferred class of the dispersing agents for use in the organic pigment dispersions are those obtained by reacting chloromethylated copper phthalocyanine with the polymer, and particularly with a monofunctional polymer or copolymer with a terminal carboxyl group in the form of its sedium or potassium salt. The polymer or copolymer will preferably have a number average molecular weight between 1,000 and 20,000 and particularly between 2,000 and 10,000. Suitable carboxyl terminated polymers or copolymers are obtained by free radical polymerisation of unsaturated monomeric compounds such as methyl methacrylate, other esters of methacylic acid, or styrene, using an initiator containing carboxyl groups in conjunction with a transfer agent containing carboxyl groups as described in Specification No. 1,096,912, or for example by anionic polymerisation using butyl lithium

reaction with carbon dioxide. The dispersions of the invention are fluid or semi-fluid compositions containing the organic pigment in finely divided and deflocculated form, and can be used for any purpose for which dispersions of these particular solids are conventionally used. Thus the dispersions are of particular value in the manufacture of printing inks, by incorporating the dispersicns with the other components conventionally used in the manufacture of such inks. The dispersions are also of value in the manufacture of paints, for which purpose the dispersions are incorporated into conventional alkyd or other resins. Alternatively, the dispersing agents can be used in the production of dispersions of other dyestuffs, such as Acid Dyestuffs, Disperse Dyestuffs and Basic Dyestuffs, in organic liquids, such dispersions being used for the transfer printing or solvent dyeing of textiles.

of unsaturated polymerisable compounds such

as styrene, butadiene or isoprene followed by

The invention is illustrated but not limited by the following Examples in which the parts and percentages are by weight.

Carboxyl terminated addition polymer A 1,000 Parts of 2 - methoxyethanol is stirred 120 and bailed under reflux whilst a mixture of 500 parts of 2 - methoxyethanol, 500 parts of methyl methacrylate, 15 parts of thiogly-collic acid and 7.5 parts of 4,4' - azobis - (4cyanovaleric acid) is added slowly. After boil-

ing under reflux for a further 3 hours the solution is added to a ten-fold excess of water, the precipitate is filtered off, washed well with water, dried and dissolved in xylene to give a

115

60

28.8% solution. Titration of the terminal carboxyl group shows the number average molecular weight to be 2950.

Carboxyl terminated addition polymer B 480 Parts of butyl acetate are stirred and boiled under reflux under nitrogen whilst a mixture of 600 parts of styrene, 12 parts of 4,4' - azobis(4 - cyanopentanoic acid), 22 parts of thiogiycollic acid, 140 parts of 2-10 methoxyethanol and 90 parts of butyl acetate is added during 3 hours. After boiling under reflux for a further 2 hours a further 4 parts of 4,4' - azobis(4 - cyanopentanoic acid) are added and boiling continued for a further 6 15 hours, 500 Parts of the solvent are then removed by distillation and the polymer precipitated by adding the solution to 2,000 parts of methanol. The precipitate is filtered off, washed with methanol, dried and dissolved in butyl acetate to give a 54.4% solution. Titrarion of the terminal carboxyl group shows the number average molecular weight to be 3,800.

Carboxyl terminated addition polymer C
This is prepared by the method described for carboxyl terminated addition polymer B except that 48 parts of thioglycollic acid are used. The precipitated and washed polymer is dissolved in toluene instead of butyl acetate, and methanol distilled out at 40°C under reduced pressure to give a 39.0% solution in toluene. Titration of the terminal carboxyl group shows the number average molecular weight to be 2300.

Carboxyl terminated addition polymer D

This is prepared by the same method as carboxyl terminated polymer C except that only 4 parts of thioglycollic acid and 4 parts of 4,4' - azobis(4 - cyanopentanoic acid) are used in the original feed. The final solution in toluene is 31.5%. The number average molecular weight is 8600.

Carboxyl terminated addition polymer E 480 Parts of butyl acetate are stirred and boiled under reflux under nitrogen whilst a mixture of 280 parts of lauryl methacrylate. 120 parts of styrene, 12 parts of 4,4' - azobis-(4 - cyanopentanoic acid), 20 parts of thioglycollic acid and 140 parts of 2 - methoxyethanol is added during 3 hours. After boiling for a further 4 hours, a further 4 parts of 4,4' - azobis(4 - cyanopentanoic acid) is added and boiling then continued for a further 7 hours. The polymer is precipitated by adding to 3000 parts of methanol, filtered off, washed with methanol, dissolved in a petroleum fraction of boiling range 170°C to 210°C and methanol distilled out at 40°C under reduced pressure to give a 38.2% solution. The number average molecular weight is 2900.

Dispersing Agent 1
A mixture of 295 parts of the 28.8% solution of carboxyl terminated addition polymer A in xylene, 1.1 parts of a commercially available grade of cetyl trimethylammonium bromide, 1.52 parts of sodium carbonate and 6.6 parts of copper tris - (chloromethyl) - phthalocyanine is stirred for 16 hours at 138°C under a reflux condenser fitted with a trap to remove water. The resulting deep blue solution is decanted from a small quantity of solid matter. The solution contains 37.6% of crude dispersing agent.

Dispersing Agent 2
A mixture of 3 parts of copper tris - (chloromethyl) - phthalocyanine and 18.4 parts of the adduct of one molecular proportion of 2-naphthol and thirty molecular proportions of ethylene oxide is stirred at 120°C for 1 hour.

0.09 Parts of zinc chloride is added and stirring at 120°C is continued for a further 16 hours. The product forms a deep blue coloured wax on cooling. It is readily soluble in water.

Dispersing Agent 3 100.5 Parts of the 54.4% solution of carboxyl terminated addition polymer B in butyl acetate is distilled under reduced pressure to remove butyl acetate. The sticky resin is dissolved in 43.5 parts of xylene. This is removed under reduced pressure. The process is repeated using in all four proportions of xylene to remove all traces of butyl acetate. The resin is finally dissolved in 60 parts of toluene. 0.55 Part of cetyl trimethylammonium bromide, 0.76 part of sodium carbonate and 3.3 parts of copper tris(chloromethyl)phthalocyanine are added. The mixture is stirred for 16 hours at 115-120°C under a reflux condenser fitted with a trap to remove water. The product is a 47.2% solution of dispersing

Dispersing Agent 4

A mixture of 52.2 parts of a solution in toluene, containing 18.2 parts of carboxyl terminated addition polymer B, prepared by the method described in Example 5, 0.18 parts of cetyl trimethylammonium bromide, 0.25 parts of sodium carbonate and 0.73 parts of copper pentakis(chloromethyl) - phthalocyanine is stirred for 16 hours at 110—120°C under reflux condenser fitted with a trap to 110 remove water. The product is 46 parts of a 42% solution of dispersing agent.

Dispersing Agent 5

This is prepared as described for Dispersing

Dispersing Agent 5
This is prepared as described for Dispersing Agent 4 but using instead of the copper pentakis (chloromethyl)phthalocyanine, 1.25 parts of a chloromethylated p,p' - bis(6-methylbenzthiazol - 2 - yl)azobenzene containing 13.1% of chlorine. The product is 45.35 parts of a 43.8% solution of dispersing agent.

6	1,424,517		
	Dispersing Agent 6 This is prepared as described for Dispers-	Example 2 A mixture of 3 parts of β-form copper	60
5	ing Agent 4 but using instead of the copper pentaltis (chloromethyl) phthalocyanine, 2.14 parts of $1 - (\gamma - \text{chloro} - \beta - \text{hydroxypropyl-amino}) - 4 - [4' - (\beta - \text{hydroxyethoxy}) - \text{anilino}] - anthraquinone. The product is 47.2 parts of a 43.9%, solution of dispersing agent.$	phthalocyanine, 1.5 parts of Dispersing Agent 2 and 5.5 parts of water is ball milled for 16 hours to give a fluid finely divided well defloculated dispersion of the pigment.  When the adduct of 2-naphthol and ethylene exide described in Dispersing Agent 2 is used instead of Dispersing Agent 2 the result-	65
10	Dispersing Agent 7 This is prepared as described for Dispersing Agent 4 but using instead of the copper	ing mill charge is too thick to mill satisfactorily.	70
15	pentakis(chloromethyl)phthalocyanine, 2.03 parts of 2 - methyl - 4 - N,N - bis - (\$\beta\$-hydroxyethyl)amino - 4' - (N - \$\beta\$ - chloroethylsulphenamido)azobenzene. The product is 41.9 parts of a 49.3% solution of dispersing agent.	Example 3  A mixture of 3 parts of $\beta$ -form copper phthalocyanine, 1.5 parts of Dispersing Agent 2 and 10.5 parts of glacial acetic acid is ball milled for 16 hours to give a fluid, finely divided well defloccuated dispersion of the pigment.	75
20	Dispersing Agent 8 85.0 Parts of the 39.0% solution of carboxyl terminated addition polymer C in toluene is stirred whilst 0.55 part of cetyl trimethylammonium bromide, 0.76 part of sodium carbonate and 3.3 parts of copper tris(chloro-	Example 4  A mixture of 2 parts of $\beta$ -form copper phthalocyanine, 2.1 parts of the 47.2% solution of Dispersing Agent 3 and 5.9 parts of toluene is ball milled for 16 hours to give a	80
25	methyl)phthalocyanine are added. The mixture is stirred for 16 hours at 112°C under a reflux condenser fitted with a trap to remove water. The product is a 52.8%, solution of dispersing agent.	fluid, finely divided well deflocculated dispersion of the pigment.  Similar finely divided well deflocculated dispersions are obtained when the 2 parts of \(\beta\)-form copper phthalocyanine are replaced by 2 parts of any of the following:	85
30	Dispersing Agent 9 97.5 Parts of the 31.5% solution of carboxyl terminated addition polymer D in toluence is stirred whilst 0.14 part of cetyl trimethylammonium bromide, 0.19 part of sodium car-	(a) rosinated calcium toner of 1 - (2'-sulpho - 4' - methylphenylazo) - 2-naphthol - 3 - carboxylic acid. (b) the phosphomelybdotungstate of C.I.	90
35	bonate and 0.83 part of copper tris(chloro- methyl)phthalocyanine are added. The mix- ture is stirred for 16 hours at 110°C under a reflux condenser fitted with a trap to remove water. The product is a 36.5% solution of	Basic Blue 7  (c) an aluminium lake of 1,4 - dihydroxy-anthraquinone - 2 - sulphonic acid  (d) copper polychlorophthalocyanine  (e) indanthrone	95
40	Dispersing Agent 10 108 Parts of the 38.2% solution of carboxyl	<ul> <li>(f) a nickel tener of 3 - (4' - chlorophenylazo) - quinoline - 2,4 - diol</li> <li>(g) a methylated 4,5 - diaminochrysazine</li> </ul>	100
45	terminated addition polymer E in a petroleum fraction of beiling range 170° to 210°C is stirred whilst 0.55 part of cetyl trimethylammonium bromide, 0.76 part of sodium carbenate and 3.3 parts of copper tris - (chloromethyl)phthalocyanine are added. The mixture is stirred for 19 hours at 110°C, in a current of nitrogen during the first two hours, under	Example 5 A mixture of 3 parts of $\beta$ -form copper phthalccyanine, 3.58 parts of the 42% solution of Dispersing Agent 4 and 8.42 parts of toluene is ball milled for 16 hours to give a fluid, finely divided well deflectuated dispersion of the pigment.	105
50	a reflux condenser fitted with a trap to remove water. The product is a 41.0% solution of dispersing agent.  Example 1	Example 6 A mixture of 2 parts of β-form copper phthalocyanine, 4.3 parts of the 47.2% solution of Dispersing Agent 3 and 3.7 parts of toluene is ball milled for 16 hours to give a fluid force of the second seco	110
EE	A mixture of 2 parts of $\beta$ -form copper	fluid, finely divided well deflocculated dispersion of the pigment.	

Example 1

A mixture of 2 parts of β-form copper phthalocyanine, 2 parts of the 37.6% solution of Dispersing Agent 1 and 8.6 parts of chloroform is ball milled for 2 hours to give a fluid, finely divided well deflocculated dispersion of the pigment.

Example 7
A mixture of 2 parts of β-form copper phthalocyanine, 1.9 parts of the 52.8% solution of Dispersing Agent 8 and 6.1 parts of 115 toluene is ball milled for 16 hours to give a fluid, finely divided well deflocculated dispersion of the pigment.

Example 8

A mixture of 2 parts of \$\beta\$-form copper phthalocyanine, 2.7 parts of the 36.5% solution of Dispersing Agent 9 and 4.3 parts of toluene is ball milled for 16 hours to give a fluid, finely divided well deflocculated dispersion of the pigment.

Example 9

A mixture of 2 parts of β-form copper phthalocyanine, 2.44 parts of the 41.0% solution of Dispersing Agent 10 and 5.56 parts of 15 White Spirit is ball milled for 16 hours to give a fluid, finely divided and well defloculated dispersion of the pigment.

WHAT WE CLAIM IS: -

 Dispersions of an organic pigment in a solvent medium which contains dissolved therein a dispersing agent of the formula

## $D - (Z - R)_n$

wherein D is the radical of a dyestuff which is attached to Z through a carbon atom of an aromatic ring present in D; Z is a divalent bridging group; n is a positive integer having a value of from 1 to 8; and R is the residue of an optionally substituted addition polymer chain.

 2. Dispersions of an organic pigment as claimed in Claim 1 wherein the radical D is a phthalocyanine radical.

 Dispersions of an organic pigment as claimed in Claim 1 or Claim 2 wherein the
 radical D is free from carboxylic or sulphonic acid groups. 4. Dispersions of an organic pigment as claimed in any one of Claims 1 to 3 wherein 7 is

-СH<sub>я</sub>---,

40

-NH-CH2-CHOHCH2-

ลกส์

## -SO<sub>2</sub>-NH-CH<sub>2</sub>CH<sub>2</sub>-

5. Dispersions of an organic pigment as claimed in any one of Claims 1 to 4 wherein R contains a solvatable polymer chain.

6. Dispersions of an organic pigment as claimed in any one of Claims 1 to 5 wherein R contains a polymer or co-polymer of an ethylenically unsaturated monomer.

 Dispersions of an organic pigment as claimed in any one of Claims 1 to 5 wherein R contains a polyalkylene oxide.

8. Dispersions of an organic pigment as claimed in any one of Claims 1 to 7 wherein the solvent medium is an organic solvent.

 Dispersions of an organic pigment as claimed in any one of Claims 1 to 7 wherein the solvent medium is an inorganic solvent.

10. Dispersions of an organic pigment as claimed in any one of Claims 1 to 9 wherein the organic pigment is copper phthalocyanine or a nuclear halogenated derivative thereof.

11. Printing inks or paints containing dispersions of organic pigments as claimed in any one of Claims 1—10.

12. Dispersions of organic pigments as claimed in any one of Claims 1 to 10 substantially as described herein with reference to any one of Examples 1 to 9.

H. P. W. HUGGILL, Agent for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1976.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

55

60

70